Median dual cell 2D

August 22, 2007

1 Equations

1.1 Mass conservation

$$\frac{\partial c_i}{\partial t} = -\vec{\nabla}.\vec{N}_i + R_i \tag{1}$$

with

$$\vec{N}_i = c_i\vec{v} - \sum_j D_{ij}\vec{\nabla}c_j - w_i c_i \vec{\nabla}U \tag{2}$$

1.2 Poisson's equation

$$\vec{\nabla}^2 U + \frac{F}{\epsilon}\sum_i z_i c_i = 0 \tag{3}$$

1.3 Butler-Volmer kinetics

$$v = k_{ox}\exp\left[\frac{\alpha_{ox}nF}{RT}(V-U)\right]c_{red} - k_{red}\exp\left[-\frac{\alpha_{red}nF}{RT}(V-U)\right]c_{ox} \tag{4}$$

2 Element matrix

2.1 Convection

2.1.1 Fluctuation in node

$$\Delta c_i^m = \int_{S^m} -\vec{v}.\vec{\nabla}c_i dS$$

2.1.2 Element contribution to fluctuation in node

$$\vec{\mathcal{V}}^1 = 22\vec{v}^1 + 7\vec{v}^2 + 7\vec{v}^3$$

$$\vec{\mathcal{V}}^2 = 7\vec{v}^1 + 22\vec{v}^2 + 7\vec{v}^3$$

$$\vec{\mathcal{V}}^3 = 7\vec{v}^1 + 7\vec{v}^2 + 22\vec{v}^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{1}{216} \left[\begin{array}{ccc} \vec{\mathcal{V}}^1.\vec{n}^1 & \vec{\mathcal{V}}^1.\vec{n}^2 & \vec{\mathcal{V}}^1.\vec{n}^3 \\ \vec{\mathcal{V}}^2.\vec{n}^1 & \vec{\mathcal{V}}^2.\vec{n}^2 & \vec{\mathcal{V}}^2.\vec{n}^3 \\ \vec{\mathcal{V}}^3.\vec{n}^1 & \vec{\mathcal{V}}^3.\vec{n}^2 & \vec{\mathcal{V}}^3.\vec{n}^3 \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ c_i^2 \\ c_i^3 \end{array} \right\} \tag{5}$$

2.1.3 Examples: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array} \right\} = \left[\begin{array}{ccccccccc} V^{11} & 0 & 0 & V^{12} & 0 & 0 & V^{13} & 0 & 0 \\ 0 & V^{11} & 0 & 0 & V^{12} & 0 & 0 & V^{13} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ V^{21} & 0 & 0 & V^{22} & 0 & 0 & V^{23} & 0 & 0 \\ 0 & V^{21} & 0 & 0 & V^{22} & 0 & 0 & V^{23} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ V^{31} & 0 & 0 & V^{32} & 0 & 0 & V^{33} & 0 & 0 \\ 0 & V^{31} & 0 & 0 & V^{32} & 0 & 0 & V^{33} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array} \right\} \tag{6}$$

with

$$V^{mn} = \frac{\vec{\mathcal{V}}^m.\vec{n}^n}{216}$$

2.2 Diffusion

2.2.1 Fluctuation in node

$$\begin{aligned} \Delta c_i^m &= \int_{S^m} \vec{\nabla}.\left(\sum_j D_{ij}\vec{\nabla}c_j\right) dS \\ &= -\int_{\partial S^m} \left(\sum_j D_{ij}\vec{\nabla}c_j\right).d\vec{n} \end{aligned}$$

2.2.2 Element contribution to fluctuation in node

Assume that D_{ij} varies linearly.

$$\vec{\mathcal{D}}_{ij}^1 = 5\vec{n}^1 D_{ij}^1 + \left(3\vec{n}^1 - \vec{n}^2\right) D_{ij}^2 + \left(3\vec{n}^1 - \vec{n}^3\right) D_{ij}^3$$

$$\vec{\mathcal{D}}_{ij}^2 = 5\vec{n}^2 D_{ij}^2 + \left(3\vec{n}^2 - \vec{n}^3\right) D_{ij}^3 + \left(3\vec{n}^2 - \vec{n}^1\right) D_{ij}^1$$

$$\vec{\mathcal{D}}_{ij}^3 = 5\vec{n}^3 D_{ij}^3 + \left(3\vec{n}^3 - \vec{n}^1\right) D_{ij}^1 + \left(3\vec{n}^3 - \vec{n}^2\right) D_{ij}^2$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = -\frac{1}{48S} \sum_j \left[\begin{array}{ccc} \vec{\mathcal{D}}_{ij}^1.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^1.\vec{n}^2 & \vec{\mathcal{D}}_{ij}^1.\vec{n}^3 \\ \vec{\mathcal{D}}_{ij}^2.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^2.\vec{n}^2 & \vec{\mathcal{D}}_{ij}^2.\vec{n}^3 \\ \vec{\mathcal{D}}_{ij}^3.\vec{n}^1 & \vec{\mathcal{D}}_{ij}^3.\vec{n}^2 & \vec{\mathcal{D}}_{ij}^3.\vec{n}^3 \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_j^2 \\ c_j^3 \end{array} \right\} \tag{7}$$

2.2.3 Example: binary electrolyte

$$\left\{\begin{array}{c}\Delta c_A^1\\ \Delta c_B^1\\ \Delta U^1\\ \Delta c_A^2\\ \Delta c_B^2\\ \Delta U^2\\ \Delta c_A^3\\ \Delta c_B^3\\ \Delta U^3\end{array}\right\} = \left[\begin{array}{ccccccccc} D_{AA}^{11} & D_{AB}^{11} & 0 & D_{AA}^{12} & D_{AB}^{12} & 0 & D_{AA}^{13} & D_{AB}^{13} & 0\\ D_{BA}^{11} & D_{BB}^{11} & 0 & D_{BA}^{12} & D_{BB}^{12} & 0 & D_{BA}^{13} & D_{BB}^{13} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ D_{AA}^{21} & D_{AB}^{21} & 0 & D_{AA}^{22} & D_{AB}^{22} & 0 & D_{AA}^{23} & D_{AB}^{23} & 0\\ D_{BA}^{21} & D_{BB}^{21} & 0 & D_{BA}^{22} & D_{BB}^{22} & 0 & D_{BA}^{23} & D_{BB}^{23} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ D_{AA}^{31} & D_{AB}^{31} & 0 & D_{AA}^{32} & D_{AB}^{32} & 0 & D_{AA}^{33} & D_{AB}^{33} & 0\\ D_{BA}^{31} & D_{BB}^{31} & 0 & D_{BA}^{32} & D_{BB}^{32} & 0 & D_{BA}^{33} & D_{BB}^{33} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right] \left\{\begin{array}{c} c_A^1\\ c_B^1\\ U^1\\ c_A^2\\ c_B^2\\ U^2\\ c_A^3\\ c_B^3\\ U^3\end{array}\right\} \tag{8}$$

with

$$D_{ij}^{mn} = -\frac{\vec{\mathcal{D}}_{ij}^{m}.\vec{n}^{n}}{48S}$$

2.3 Migration

2.3.1 Fluctuation in node

$$\begin{aligned}\Delta c_i^m &= \int_{S^m} \vec{\nabla}.\left(w_i c_i \vec{\nabla} U\right) dS\\ &= -\int_{\partial S^m} \left(w_i c_i \vec{\nabla} U\right).d\vec{n}\end{aligned}$$

2.3.2 Element contribution to fluctuation in node

Assume that w_i varies linearly.

$$\vec{\mathcal{M}}_i^1 = \vec{\mathcal{W}}_i^{11} c_i^1 + \vec{\mathcal{W}}_i^{12} c_i^2 + \vec{\mathcal{W}}_i^{13} c_i^3$$

$$\vec{\mathcal{M}}_i^2 = \vec{\mathcal{W}}_i^{21} c_i^1 + \vec{\mathcal{W}}_i^{22} c_i^2 + \vec{\mathcal{W}}_i^{23} c_i^3$$

$$\vec{\mathcal{M}}_i^3 = \vec{\mathcal{W}}_i^{31} c_i^1 + \vec{\mathcal{W}}_i^{32} c_i^2 + \vec{\mathcal{W}}_i^{33} c_i^3$$

$$\vec{\mathcal{W}}_i^{11} = 19\vec{n}^1 w_i^1 + \left(11\vec{n}^1 - 4\vec{n}^2\right) w_i^2 + \left(11\vec{n}^1 - 4\vec{n}^3\right) w_i^3$$

$$\vec{\mathcal{W}}_i^{12} = \left(11\vec{n}^1 - 4\vec{n}^2\right) w_i^1 + \left(9\vec{n}^1 - 5\vec{n}^2\right) w_i^2 + 7\vec{n}^1 w_i^3$$

$$\vec{\mathcal{W}}_i^{13} = \left(11\vec{n}^1 - 4\vec{n}^3\right) w_i^1 + 7\vec{n}^1 w_i^2 + \left(9\vec{n}^1 - 5\vec{n}^3\right) w_i^3$$

$$\vec{\mathcal{W}}_i^{21} = \left(9\vec{n}^2 - 5\vec{n}^1\right) w_i^1 + \left(11\vec{n}^2 - 4\vec{n}^1\right) w_i^2 + 7\vec{n}^2 w_i^3$$

$$\vec{\mathcal{W}}_i^{22} = \left(11\vec{n}^2 - 4\vec{n}^1\right) w_i^1 + 19\vec{n}^2 w_i^2 + \left(11\vec{n}^2 - 4\vec{n}^3\right) w_i^3$$

$$\vec{\mathcal{W}}_i^{23} = 7\vec{n}^2 w_i^1 + \left(11\vec{n}^2 - 4\vec{n}^3\right) w_i^2 + \left(9\vec{n}^2 - 5\vec{n}^3\right) w_i^3$$

$$\vec{\mathcal{W}}_i^{31} = \left(9\vec{n}^3 - 5\vec{n}^1\right) w_i^1 + 7\vec{n}^3 w_i^2 + \left(11\vec{n}^3 - 4\vec{n}^1\right) w_i^3$$

$$\vec{\mathcal{W}}_i^{32} = 7\vec{n}^3 w_i^1 + \left(9\vec{n}^3 - 5\vec{n}^2\right) w_i^2 + \left(11\vec{n}^3 - 4\vec{n}^2\right) w_i^3$$

$$\vec{\mathcal{W}}_i^{33} = \left(11\vec{n}^3 - 4\vec{n}^1\right) w_i^1 + \left(11\vec{n}^3 - 4\vec{n}^2\right) w_i^2 + 19\vec{n}^3 w_i^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = -\frac{1}{432S} \left[\begin{array}{ccc} \vec{\mathcal{M}}_i^1.\vec{n}^1 & \vec{\mathcal{M}}_i^1.\vec{n}^2 & \vec{\mathcal{M}}_i^1.\vec{n}^3 \\ \vec{\mathcal{M}}_i^2.\vec{n}^1 & \vec{\mathcal{M}}_i^2.\vec{n}^2 & \vec{\mathcal{M}}_i^2.\vec{n}^3 \\ \vec{\mathcal{M}}_i^3.\vec{n}^1 & \vec{\mathcal{M}}_i^3.\vec{n}^2 & \vec{\mathcal{M}}_i^3.\vec{n}^3 \end{array} \right] \left\{ \begin{array}{c} U^1 \\ U^2 \\ U^3 \end{array} \right\} \tag{9}$$

2.3.3 Example: binary electrolyte

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array} \right\} = \left[\begin{array}{ccccccccc} 0 & 0 & M_A^{11} & 0 & 0 & M_A^{12} & 0 & 0 & M_A^{13} \\ 0 & 0 & M_B^{11} & 0 & 0 & M_B^{12} & 0 & 0 & M_B^{13} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{21} & 0 & 0 & M_A^{22} & 0 & 0 & M_A^{23} \\ 0 & 0 & M_B^{21} & 0 & 0 & M_B^{22} & 0 & 0 & M_B^{23} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & M_A^{31} & 0 & 0 & M_A^{32} & 0 & 0 & M_A^{33} \\ 0 & 0 & M_B^{31} & 0 & 0 & M_B^{32} & 0 & 0 & M_B^{33} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array} \right] \left\{ \begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array} \right\} \tag{10}$$

with

$$M_i^{mn} = -\frac{\vec{\mathcal{M}}_A^m.\vec{n}^n}{432S}$$

2.4 Homogeneous reactions

2.4.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

- Monomolecular

$$v = kc_j$$

$$\Delta c_i^m = \int_{S^m} kc_j dS$$

- Bimolecular

$$v = kc_jc_k$$

$$\Delta c_i^m = \int_{S^m} kc_jc_k dS$$

2.4.2 Element contribution to fluctuation in node

Assume that k varies linearly.

- Monomolecular

$$\mathcal{H}_j^{11} = 170k^1 + 47k^2 + 47k^3$$

$$\mathcal{H}_j^{12} = 47k^1 + 23k^2 + 14k^3$$

$$\mathcal{H}_j^{13} = 47k^1 + 14k^2 + 23k^3$$

$$\mathcal{H}_j^{21} = 23k^1 + 47k^2 + 14k^3$$

$$\mathcal{H}_j^{22} = 47k^1 + 170k^2 + 47k^3$$

$$\mathcal{H}_j^{23} = 14k^1 + 47k^2 + 23k^3$$

$$\mathcal{H}_j^{31} = 23k^1 + 14k^2 + 47k^3$$

$$\mathcal{H}_j^{32} = 14k^1 + 23k^2 + 47k^3$$

$$\mathcal{H}_j^{33} = 47k^1 + 47k^2 + 170k^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{S}{1296} \left[\begin{array}{ccc} \mathcal{H}_j^{11} & \mathcal{H}_j^{12} & \mathcal{H}_j^{13} \\ \mathcal{H}_j^{21} & \mathcal{H}_j^{22} & \mathcal{H}_j^{23} \\ \mathcal{H}_j^{31} & \mathcal{H}_j^{32} & \mathcal{H}_j^{33} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_j^2 \\ c_j^3 \end{array} \right\} \tag{11}$$

- Bimolecular

$$\mathcal{K}^{111} = 1150k^1 + 275k^2 + 275k^3$$

$$\mathcal{K}^{222} = 275k^1 + 1150k^2 + 275k^3$$

$$\mathcal{K}^{333} = 275k^1 + 275k^2 + 1150k^3$$

$$\mathcal{K}^{112} = \mathcal{K}^{121} = 275k^1 + 123k^2 + 72k^3$$

$$\mathcal{K}^{113} = \mathcal{K}^{131} = 275k^1 + 72k^2 + 123k^3$$

$$\mathcal{K}^{221} = \mathcal{K}^{212} = 123k^1 + 275k^2 + 72k^3$$

$$\mathcal{K}^{223} = \mathcal{K}^{232} = 72k^1 + 275k^2 + 123k^3$$

$$\mathcal{K}^{331} = \mathcal{K}^{313} = 123k^1 + 72k^2 + 275k^3$$

$$\mathcal{K}^{332} = \mathcal{K}^{323} = 72k^1 + 123k^2 + 275k^3$$

$$\mathcal{K}^{122} = 123k^1 + 73k^2 + 34k^3$$

$$\mathcal{K}^{133} = 123k^1 + 34k^2 + 73k^3$$

$$\mathcal{K}^{211} = 73k^1 + 123k^2 + 34k^3$$

$$\mathcal{K}^{233} = 34k^1 + 123k^2 + 73k^3$$

$$\mathcal{K}^{311} = 73k^1 + 34k^2 + 123k^3$$

$$\mathcal{K}^{322} = 43k^1 + 73k^2 + 123k^3$$

$$\mathcal{K}^{123} = \mathcal{K}^{132} = 72k^1 + 34k^2 + 34k^3$$

$$\mathcal{K}^{213} = \mathcal{K}^{231} = 34k^1 + 72k^2 + 34k^3$$

$$\mathcal{K}^{312} = \mathcal{K}^{321} = 34k^1 + 34k^2 + 72k^3$$

$$\mathcal{H}_j^{11} = \mathcal{K}^{111} c_k^1 + \mathcal{K}^{112} c_k^2 + \mathcal{K}^{113} c_k^3$$

$$\mathcal{H}_j^{12} = \mathcal{K}^{121} c_k^1 + \mathcal{K}^{122} c_k^2 + \mathcal{K}^{123} c_k^3$$

$$\mathcal{H}_j^{13} = \mathcal{K}^{131} c_k^1 + \mathcal{K}^{132} c_k^2 + \mathcal{K}^{133} c_k^3$$

$$\mathcal{H}_j^{21} = \mathcal{K}^{211} c_k^1 + \mathcal{K}^{212} c_k^2 + \mathcal{K}^{213} c_k^3$$

$$\mathcal{H}_j^{22} = \mathcal{K}^{221} c_k^1 + \mathcal{K}^{222} c_k^2 + \mathcal{K}^{223} c_k^3$$

$$\mathcal{H}_j^{23} = \mathcal{K}^{231} c_k^1 + \mathcal{K}^{232} c_k^2 + \mathcal{K}^{233} c_k^3$$

$$\mathcal{H}_j^{31} = \mathcal{K}^{311} c_k^1 + \mathcal{K}^{312} c_k^2 + \mathcal{K}^{313} c_k^3$$

$$\mathcal{H}_j^{32} = \mathcal{K}^{321} c_k^1 + \mathcal{K}^{322} c_k^2 + \mathcal{K}^{323} c_k^3$$

$$\mathcal{H}_j^{33} = \mathcal{K}^{331} c_k^1 + \mathcal{K}^{332} c_k^2 + \mathcal{K}^{333} c_k^3$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{S}{25920} \left[\begin{array}{cccccc} \mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12} & \mathcal{H}_j^{13} & \mathcal{H}_k^{13} \\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22} & \mathcal{H}_j^{23} & \mathcal{H}_k^{23} \\ \mathcal{H}_j^{31} & \mathcal{H}_k^{31} & \mathcal{H}_j^{32} & \mathcal{H}_k^{32} & \mathcal{H}_j^{33} & \mathcal{H}_k^{33} \end{array} \right] \left\{ \begin{array}{c} c_j^1 \\ c_k^1 \\ c_j^2 \\ c_k^2 \\ c_j^3 \\ c_k^3 \end{array} \right\} \tag{12}$$

2.4.3 Example: monomolecular-monomolecular reversible reaction $A \rightleftharpoons B$

$$v = k_f c_A - k_b c_B$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array}\right\} = \left[\begin{array}{ccccccccc} -H_A^{11} & H_B^{11} & 0 & -H_A^{12} & H_B^{12} & 0 & -H_A^{13} & H_B^{13} & 0 \\ H_A^{11} & -H_B^{11} & 0 & H_A^{12} & -H_B^{12} & 0 & H_A^{13} & -H_B^{13} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -H_A^{21} & H_B^{21} & 0 & -H_A^{22} & H_B^{22} & 0 & -H_A^{23} & H_B^{23} & 0 \\ H_A^{21} & -H_B^{21} & 0 & H_A^{22} & -H_B^{22} & 0 & H_A^{23} & -H_B^{23} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -H_A^{31} & H_B^{31} & 0 & -H_A^{32} & H_B^{32} & 0 & -H_A^{33} & H_B^{33} & 0 \\ H_A^{31} & -H_B^{31} & 0 & H_A^{32} & -H_B^{32} & 0 & H_A^{33} & -H_B^{33} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right] \left\{\begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array}\right\} \tag{13}$$

with for the forward reaction (replace k by k_f in the formulae!)

$$H_A^{mn} = \frac{S}{1296}\mathcal{H}_A^{mn}$$

and for the backward reaction (replace k by k_b in the formulae!)

$$H_B^{mn} = \frac{S}{1296}\mathcal{H}_B^{mn}$$

2.5 Poisson's equation

2.5.1 Fluctuation in node

$$\begin{array}{rcl} \Delta U^m & = & \int_{S^m} \vec{\nabla}^2 U dS + \int_{S^m} \frac{F}{\epsilon} \sum_i z_i c_i dS \\ & = & -\int_{\partial S^m} \vec{\nabla} U . d\vec{n} + \sum_i \frac{z_i F}{\epsilon} \int_{S^m} c_i dS \end{array}$$

2.5.2 Element contribution to fluctuation in node

$$\left\{\begin{array}{c} \Delta U^1 \\ \Delta U^2 \\ \Delta U^3 \end{array}\right\} = \left[\begin{array}{cccccc} \frac{22S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^1}{4S} & \frac{7S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^2}{4S} & \frac{7S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^1.\vec{n}^3}{4S} \\ \frac{7S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^1}{4S} & \frac{22S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^2}{4S} & \frac{7S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^2.\vec{n}^3}{4S} \\ \frac{7S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^1}{4S} & \frac{7S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^2}{4S} & \frac{22S}{108}\frac{z_iF}{\epsilon} & -\frac{\vec{n}^3.\vec{n}^3}{4S} \end{array}\right] \left\{\begin{array}{c} c_i^1 \\ U^1 \\ c_i^2 \\ U^2 \\ c_i^3 \\ U^3 \end{array}\right\} \tag{14}$$

2.5.3 Example: binary electrolyte

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \\ \Delta c_A^3 \\ \Delta c_B^3 \\ \Delta U^3 \end{array}\right\} = \left[\begin{array}{ccccccccc} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 22Z_A & 22Z_B & n^{11} & 7Z_A & 7Z_B & n^{12} & 7Z_A & 7Z_B & n^{13} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 7Z_A & 7Z_B & n^{21} & 22Z_A & 22Z_B & n^{22} & 7Z_A & 7Z_B & n^{23} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 7Z_A & 7Z_B & n^{31} & 7Z_A & 7Z_B & n^{32} & 22Z_A & 22Z_B & n^{33} \end{array}\right] \left\{\begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \\ c_A^3 \\ c_B^3 \\ U^3 \end{array}\right\} \tag{15}$$

with

$$Z_i = \frac{S}{108}\frac{z_i F}{\epsilon}$$

$$n^{mn} = -\frac{\vec{n}^m.\vec{n}^n}{4S}$$

2.6 Time

2.6.1 Fluctuation in node

$$\Delta c_i^m = \int_{S^m} \frac{\partial c_i}{\partial t} dS$$

2.6.2 Element contribution to fluctuation in node

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = \frac{S}{108} \left[\begin{array}{ccc} 22 & 7 & 7 \\ 7 & 22 & 7 \\ 7 & 7 & 22 \end{array} \right] \left\{ \begin{array}{c} \frac{\partial c_i^1}{\partial t} \\ \frac{\partial c_i^2}{\partial t} \\ \frac{\partial c_i^3}{\partial t} \end{array} \right\} \tag{16}$$

3 Boundary element vector

3.1 Electrode reactions

3.1.1 Fluctuation in node

$$R_i = \sum_r s_{i,r} v_r$$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_{red} - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_{ox}$$

$$\Delta c_i^m = \int_{L^m} R_i dL$$

3.1.2 Boundary element contribution to fluctuation in node

Assume that the normal flux varies linearly on the boundary.

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array} \right\} = \frac{L}{8} \left\{ \begin{array}{c} 3R_i^1 + R_i^2 \\ R_i^1 + 3R_i^2 \end{array} \right\} \tag{17}$$

3.1.3 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$v = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_B - k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_A$$

$$R_A = -v$$

$$R_B = v$$

$$\left\{ \begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array} \right\} = \left\{ \begin{array}{c} -\frac{L}{8}\left(3v^1 + v^2\right) \\ \frac{L}{8}\left(3v^1 + v^2\right) \\ 0 \\ -\frac{L}{8}\left(v^1 + 3v^2\right) \\ \frac{L}{8}\left(v^1 + 3v^2\right) \\ 0 \end{array} \right\} \tag{18}$$

4 Element jacobian

4.1 Convection

Zero contribution.

4.2 Diffusion

Zero contribution (approximately).

4.3 Migration

4.3.1 Element contribution to fluctuation in node

$$\vec{\nabla} U = \frac{\vec{n}^1 U^1 + \vec{n}^2 U^2 + \vec{n}^3 U^3}{2S}$$

$$\left\{ \begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \\ \Delta c_i^3 \end{array} \right\} = -\frac{\vec{\nabla} U}{216} . \left[\begin{array}{ccc} \vec{\mathcal{W}}_i^{11} & \vec{\mathcal{W}}_i^{12} & \vec{\mathcal{W}}_i^{13} \\ \vec{\mathcal{W}}_i^{21} & \vec{\mathcal{W}}_i^{22} & \vec{\mathcal{W}}_i^{23} \\ \vec{\mathcal{W}}_i^{31} & \vec{\mathcal{W}}_i^{32} & \vec{\mathcal{W}}_i^{33} \end{array} \right] \left\{ \begin{array}{c} c_i^1 \\ c_i^2 \\ c_i^3 \end{array} \right\} \tag{19}$$

4.3.2 Example: binary electrolyte

$$\left\{\begin{array}{c}\Delta c_A^1\\ \Delta c_B^1\\ \Delta U^1\\ \Delta c_A^2\\ \Delta c_B^2\\ \Delta U^2\\ \Delta c_A^3\\ \Delta c_B^3\\ \Delta U^3\end{array}\right\} = \begin{bmatrix} \tilde{M}_A^{11} & 0 & 0 & \tilde{M}_A^{12} & 0 & 0 & \tilde{M}_A^{13} & 0 & 0\\ 0 & \tilde{M}_B^{11} & 0 & 0 & \tilde{M}_B^{12} & 0 & 0 & \tilde{M}_B^{13} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ \tilde{M}_A^{21} & 0 & 0 & \tilde{M}_A^{22} & 0 & 0 & \tilde{M}_A^{23} & 0 & 0\\ 0 & \tilde{M}_B^{21} & 0 & 0 & \tilde{M}_B^{22} & 0 & 0 & \tilde{M}_B^{23} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ \tilde{M}_A^{31} & 0 & 0 & \tilde{M}_A^{32} & 0 & 0 & \tilde{M}_A^{33} & 0 & 0\\ 0 & \tilde{M}_B^{31} & 0 & 0 & \tilde{M}_B^{32} & 0 & 0 & \tilde{M}_B^{33} & 0\\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \left\{\begin{array}{c} c_A^1\\ c_B^1\\ U^1\\ c_A^2\\ c_B^2\\ U^2\\ c_A^3\\ c_B^3\\ U^3\end{array}\right\} \tag{20}$$

with

$$\tilde{M}_i^{mn} = -\vec{\nabla}U.\frac{\vec{\mathcal{W}}_i^{mn}}{216}$$

4.4 Homogeneous reactions

4.4.1 Element contribution to fluctuation in node

- Monomolecular

Zero contribution (approximately).

- Bimolecular

Because of the symmetry it is the same contribution.

$$\left\{\begin{array}{c}\Delta c_i^1\\ \Delta c_i^2\\ \Delta c_i^3\end{array}\right\} = \frac{S}{25920}\begin{bmatrix} \mathcal{H}_j^{11} & \mathcal{H}_k^{11} & \mathcal{H}_j^{12} & \mathcal{H}_k^{12} & \mathcal{H}_j^{13} & \mathcal{H}_k^{13}\\ \mathcal{H}_j^{21} & \mathcal{H}_k^{21} & \mathcal{H}_j^{22} & \mathcal{H}_k^{22} & \mathcal{H}_j^{23} & \mathcal{H}_k^{23}\\ \mathcal{H}_j^{31} & \mathcal{H}_k^{31} & \mathcal{H}_j^{32} & \mathcal{H}_k^{32} & \mathcal{H}_j^{33} & \mathcal{H}_k^{33} \end{bmatrix} \left\{\begin{array}{c} c_j^1\\ c_k^1\\ c_j^2\\ c_k^2\\ c_j^3\\ c_k^3\end{array}\right\} \tag{21}$$

4.5 Poisson's equation

Zero contribution.

4.6 Time

Zero contribution.

5 Boundary element jacobian

5.1 Electrode reactions

5.1.1 Partial derivatives

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox} nF}{RT} k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_{red} - \frac{\alpha_{red} nF}{RT} k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_{ox}$$

$$\frac{\partial v}{\partial c_{ox}} = -k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_{red}} = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]$$

$$\left\{\begin{array}{c} \Delta c_i^1 \\ \Delta c_i^2 \end{array}\right\} = \frac{L}{8}\left[\begin{array}{cccc} 3\frac{\partial R_i^1}{\partial c_j^1} & 3\frac{\partial R_i^1}{\partial U^1} & \frac{\partial R_i^2}{\partial c_j^2} & \frac{\partial R_i^2}{\partial U^2} \\ \frac{\partial R_i^1}{\partial c_j^1} & \frac{\partial R_i^1}{\partial U^1} & 3\frac{\partial R_i^2}{\partial c_j^2} & 3\frac{\partial R_i^2}{\partial U^2} \end{array}\right]\left\{\begin{array}{c} c_j^1 \\ U^1 \\ c_j^2 \\ U^2 \end{array}\right\} \tag{22}$$

5.1.2 Example: binary electrolyte, $A \rightleftharpoons B + ne^-$

$$\frac{\partial v}{\partial U} = -\frac{\alpha_{ox} nF}{RT} k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right] c_B - \frac{\alpha_{red} nF}{RT} k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right] c_A$$

$$\frac{\partial v}{\partial c_A} = -k_{red} \exp\left[-\frac{\alpha_{red} nF}{RT}(V-U)\right]$$

$$\frac{\partial v}{\partial c_B} = k_{ox} \exp\left[\frac{\alpha_{ox} nF}{RT}(V-U)\right]$$

$$\left\{\begin{array}{c} \Delta c_A^1 \\ \Delta c_B^1 \\ \Delta U^1 \\ \Delta c_A^2 \\ \Delta c_B^2 \\ \Delta U^2 \end{array}\right\} = \left[\begin{array}{cccccc} -3\tilde{C}_A^1 & -3\tilde{C}_B^1 & -3\tilde{U}^1 & -\tilde{C}_A^2 & -\tilde{C}_B^2 & -\tilde{U}^2 \\ 3\tilde{C}_A^1 & 3\tilde{C}_B^1 & 3\tilde{U}^1 & \tilde{C}_A^2 & \tilde{C}_B^2 & \tilde{U}^2 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -\tilde{C}_A^1 & -\tilde{C}_B^1 & -\tilde{U}^1 & -3\tilde{C}_A^2 & -3\tilde{C}_B^2 & -3\tilde{U}^2 \\ \tilde{C}_A^1 & \tilde{C}_B^1 & \tilde{U}^1 & 3\tilde{C}_A^2 & 3\tilde{C}_B^2 & 3\tilde{U}^2 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right]\left\{\begin{array}{c} c_A^1 \\ c_B^1 \\ U^1 \\ c_A^2 \\ c_B^2 \\ U^2 \end{array}\right\} \tag{23}$$

with

$$\tilde{C}_i^m = \frac{L}{8}\frac{\partial v^m}{\partial c_i^m}$$

$$\tilde{U}^m = \frac{L}{8}\frac{\partial v^m}{\partial U^m}$$